

Heavy Vehicle Propulsion Materials

Microstructural Changes in NO_x Trap Materials Under Lean and Rich Conditions at High Temperatures

Background

The introduction of diesel engine-based, heavy-duty trucks and passenger vehicles depends upon the successful development of a strategy to treat nitrogen oxide (NO_x) emissions. A catalyst or combination of catalysts that can convert NO_x into inert gases under oxidizing conditions over a complete range of exhaust temperatures does not presently exist. Among NO_x treatment strategies, lean traps (LNT) are the most likely candidates for early deployment because they are consumer transparent (no action needed on the part of consumers), and they can be system-integrated into current vehicle control strategies.

The basic components of NO_x traps are identical to three-way catalysts. The NO_x traps derived from advanced three-way catalysts are two-layer systems on a honeycomb substrate with the inner layer based on platinum-alumina and the outer layer on rhodium-ceria-zirconia. In addition, there is high baria content (the upper limit being close to 20 percent)

in the alumina layer. Fresh NO_x traps work very well but cannot sustain their high efficiency over the lifetime of vehicles.

The performance deterioration in NO_x traps is believed to be caused by aging due to high-temperature operation and sulfation-desulfation cycles necessitated by the sulfur oxides in the emissions from the oxidation of sulfur in fuel.

Technology

Studies of the microstructural changes that occurred in a supplier lean NO_x trap system (two layers: Pt/BaO-Al₂O₃ and CeO₂-ZrO₂) upon aging on 1) a pulsator at Ford, 2) dyno at Ford, and 3) on vehicles in gasoline DISI engines in Europe, show that the sintering and migration of precious metals and migration of barium leads to reduced precious metal-adsorber surface area available for NO_x adsorption in lean cycles.



Figure 1. Ex-situ reactor allows rapid screening of catalysts for microstructural changes under simulated operating conditions and accelerated aging conditions.

Benefits

- Better understanding of catalyst response to thermal cycling for desulfation.
- Correlation of microstructure changes with catalyst performance facilitates rapid development of durable, effective catalysts.



In order to design a thermally durable NO_x trap, there is a need to understand the changes in the microstructure of materials that occur during various modes of operation (lean, rich, and lean-rich cycles). Oak Ridge National Laboratory (ORNL) scientists have designed an ex-situ reactor system that allows for the rapid screening of microstructural changes in catalyst materials upon extended exposure to operating conditions or accelerated aging conditions using simulated exhaust (see Figure 1).

For rapid screening, the catalyst samples are deposited on specially designed transmission electron microscopy grids. The sample grid is then transferred to a TEM and several areas of sample are imaged. The grid is then placed in the ex-situ reactor and exposed to lean, rich, or lean-rich cycle using a simulated exhaust gas stream. The samples are transferred to TEM and the original areas are examined again. This approach allows us to accurately monitor microstructural changes in a

sample and eliminates averaging effects common to several other techniques (e.g., spectroscopic methods, XRD, EXAFS, XANES etc.).

For example, the accelerated aging of model catalyst, 2% Pt-98% [10% CeO_2 - ZrO_2 -90% (2% La_2O_3 -98% $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$)], was carried out using simulated exhaust under a lean-rich cycle. Interestingly, Pt sintering was evident after only 4 hours of sample treatment under accelerated aging conditions. A gradual growth in Pt particles in the 2.0-5.0 nm range was seen after each additional four hours of treatment.

Status

The efforts to correlate the microstructural changes with catalyst performance are in progress. The results will allow us to rapidly screen samples for microstructural changes and thereby for performance facilitating rapid development of durable catalysts.

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